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Latitudinal, vertical, and seasonal variations of C₁-C₄ alkyl nitrates in the troposphere over the Pacific Ocean during PEM-Tropics A and B: Oceanic and continental sources

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[1] We present concentration distributions of C₁-C₄ alkyl nitrates observed during the NASA airborne campaigns Pacific Exploratory Mission (PEM) -Tropics A (September–October 1996) and PEM-Tropics B (March–April 1999). The total geographic range for PEM-Tropics A was 45°N–72°S latitude and 153°E–75°W longitude, and for PEM-Tropics B was 40°N–36°S latitude and 149°E–75°W longitude. The maximum altitude for these missions was 12 km. These experiments provide the most extensive set of tropospheric measurements collected to date over the tropical Pacific Ocean. We observed high methyl nitrate (MeONO₂, CH₃ONO₂) mixing ratios (approximately 50 pptv) at low altitudes in a latitude band between 8°N to 13°S stretching across the equatorial Pacific, illustrating the oceanic source of MeONO₂. This source may be associated with the high-nutrient, low-chlorophyll character of equatorial Pacific waters. We discuss MeONO₂ and ethyl nitrate (EtONO₂, C₂H₅ONO₂), whose abundance is dominated by equatorial oceanic sources, 2-Propyl nitrate (2-PrONO₂, 2-C₃H₇ONO₂), which has significant oceanic and northern hemispheric (NH) sources associated with urban/industrial hydrocarbon emissions, and 2-butyl nitrate (2-BuONO₂, 2-C₄H₉ONO₂), which has mostly NH sources. PEM-Tropics A and B resulted in remarkably similar equatorial mixing ratios. The excellent correlations between MeONO₂ and the other alkyl nitrates in this region produced comparable correlation slopes between the two expeditions. By contrast, NH air masses influenced by urban/industrial emissions typically exhibited much lower MeONO₂:EtONO₂, MeONO₂:2-PrONO₂, and MeONO₂:2-BuONO₂ ratios. These relationships can be useful as a diagnostic of air mass origin. North of 10°N, the springtime PEM-Tropics B mixing ratios of C₂-C₄ alkyl nitrates were many-fold higher at low-mid altitudes than for late summer PEM-Tropics A, consistent with strong continental outflow of NMHC precursors during spring.

INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; **KEYWORDS:** Airborne measurements, equatorial ocean emissions, organic nitrates, methyl nitrate, ethyl nitrate, butyl nitrate

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1. Introduction

[2] The heavier alkyl nitrates (>C₁) are known to form photochemically in the atmosphere following the hydroxyl radical initiated oxidation of alkanes in the presence of NO_x

[Darnall *et al.*, 1976; Atkinson *et al.*, 1982; Roberts, 1990]. Also, measurements in the remote atmosphere have suggested an additional oceanic source of alkyl nitrates to the tropical equatorial Pacific atmosphere [Atlas *et al.*, 1993; Walega *et al.*, 1992; Blake *et al.*, 1999a]. The lightest alkyl nitrates (<C₄) are removed principally by photolysis, with OH reaction playing a progressively more important role as the hydrocarbon chain length increases [Clemshaw

et al., 1997]. Alkyl nitrates have atmospheric lifetimes ranging from about one month to several days, depending on alkyl chain length, thus long range transport is likely to play an important role in their remote tropospheric distributions [Atherton, 1989]. Until recently, few alkyl nitrate measurements had been made in the troposphere over the Pacific. Ridley *et al.* [1997] reported aircraft measurements of NMHCs and alkyl nitrates made near Hawaii. Most other measurements in the Pacific region have been made during shipboard studies, such as the Soviet-American Gases and Aerosols (SAGA-3) experiment, or at the Mauna Loa Observatory [Atlas *et al.*, 1992; Atlas and Ridley, 1996; Walega *et al.*, 1992]. For SAGA-3, Atlas *et al.* [1993] reported a broad maximum in the atmospheric mixing ratios of the C₂ and C₃ alkyl nitrates centered near the equator and concluded that there was a possible oceanic source for these alkyl nitrates related to surface water biota. However, the mechanism of production in seawater is not known [Atlas *et al.*, 1997].

[3] In August–September 1996, PEM-Tropics A provided the first detailed survey of tropospheric chemistry, including the vertical and spatial distributions of NMHCs, halocarbons, and alkyl nitrates over the South Pacific Basin [Hoell *et al.*, 1999; Blake *et al.*, 1999b, 2001]. In addition, MeONO₂ concentrations were measured in latitudinal profiles over the Pacific Ocean and during intensive aircraft sampling south of Tasmania, as part of the First Aerosol Characterization Experiment (ACE-1) in November–December 1995 [Blake *et al.*, 1999a]. Maximum ACE-1 MeONO₂ concentrations were found over the equatorial regions of the Pacific.

[4] Alkyl nitrates have relatively low reactivity compared to other components of atmospheric reactive nitrogen (NO_y) and as such are potentially important long-range carriers of NO_x to the remote troposphere. However, recent studies suggest that they typically make a relatively small contribution to the remote NO_x budget [e.g., Schultz *et al.*, 1999]. Alkyl nitrates have been of particular interest to the atmospheric measurement community as a reservoir of NO_y possibly helping to explain problems with closure of the NO_y budget [Roberts, 1995, and references therein]. Talbot *et al.* [2000] examined the NO_y budget for PEM-Tropics A and reported that in the equatorial marine boundary layer, the 50 pptv averaged alkyl nitrate sum comprised a major component (20–80%) of total NO_y. In air of tropical origin measured at Mauna Loa, Hawaii, MeONO₂ was up to 10% of NO_y [Walega *et al.*, 1992]. Recent results from coastal Antarctica indicate that RONO₂ can be a high proportion of NO_y [Jones *et al.*, 1999]. However, studies of urban/rural air masses have shown alkyl nitrates typically to contribute less than 10% of NO_y [e.g., Buhr *et al.*, 1990; Ridley *et al.*, 1990; Flocke *et al.*, 1991; Roberts *et al.*, 1996; Shepson *et al.*, 1993; O'Brien *et al.*, 1995; Talbot *et al.*, 1999].

[5] This paper presents the two most spatially extensive measurements of light alkyl nitrates ever reported. The samples were collected throughout the Pacific region during two seasons: PEM-Tropics A (August–October 1996) and PEM-Tropics B (March–April 1999). The total geographic range for PEM-Tropics A was 45°N–72°S latitude and 153°E–75°W longitude, and for PEM-Tropics B was 40°N–36°S latitude and 149°E–75°W longitude. The

maximum altitude for these missions was 12 km. The dataset is so extensive that it enables, for the first time, contour plots to be produced with latitude/longitude distributions and latitude/altitude distributions. By comparison with known biogenic and anthropogenic emissions, as well as with geographical distributions, the relative biogenic/anthropogenic source strengths of the alkyl nitrates are deduced. Since light alkyl nitrates have both oceanic emission sources and continental photochemical sources and long lifetimes, these data will be a valuable asset to the global modeling community in validating emissions, photochemistry and transport in 3-D models.

2. Experiment

[6] Sampling and analytical details can be found in Colman *et al.* [2001] so will be described here only briefly. Our “in-house” 2-liter electropolished stainless steel sampling canisters, which are conditioned and tested regularly to ensure reliability, were filled with whole air collected from beyond the laminar boundary layer of the NASA DC-8 and P-3B aircraft and pressurized to about 3.8 hPa employing a two-stage metal bellows pump (Parker MB-602XP). Approximately 140 samples were collected during a typical 8-hour DC-8 flight, and 120 canisters for each 8-hour flight aboard the P-3B. These samples were obtained roughly every 3–7 min during horizontal flight legs and 1–3 min during vertical legs. The P-3B typically flew at low levels (0.1–7.5 km) whereas the DC-8 operated at higher altitudes (5–12 km) with occasional excursions into the boundary layer. During both horizontal and vertical flight legs, our sampling duration was a minimum of 8 s at low altitude (150 m) to approximately 90 s at high altitude (12 km). Sampling time during horizontal legs was usually adjusted to be about 1 minute, corresponding to an approximate sampling distance of 8–12 km. Typical vertical sampling distances were 300 m for the DC-8, and 150 m for the P-3B.

[7] After each flight, the filled canisters were transported via courier to our laboratory at the University of California-Irvine (UCI) for analysis, which usually was completed within ten days of sample collection. The analytical procedures are detailed in Colman *et al.* [2001]. Briefly, each sample was analyzed for more than 50 trace gases comprising hydrocarbons, halocarbons, dimethyl sulfide (DMS) (PEM-Tropics B only), and alkyl nitrates [see also Sive, 1998; Simpson *et al.*, 2001; Blake *et al.*, 2001]. Two identical analytical systems sharing the same standards were operated simultaneously around the clock to improve canister turn-around time. Approximately 15% of the samples were also analyzed in the National Center for Atmospheric Research (NCAR) laboratory using GC/MS techniques. After analysis in the UCI laboratory, samples either were cryogenically transferred to NCAR canisters or the UCI canisters were analyzed directly at NCAR. The agreement between UCI and NCAR values was very good, typically with R² values better than 0.99.

[8] 1520 ± 1 cm³ (STP) of air was preconcentrated in liquid nitrogen, warmed, then quantitatively split into five streams, with each stream directed to a different column-detector combination [Colman *et al.*, 2001]. Silcosteel tubing (0.53 mm O.D.) was used to connect the columns to

the splitter boxes. The split ratio was found to be highly reproducible as long as the specific humidity of the injected air was above 2 g H₂O/kg air. For this reason, as well as to increase the stability of certain compounds in our canisters, about 2.3 kPa of water was added to each (preconditioned, evacuated) canister.

[9] The C₁-C₄ alkyl nitrates were separated analytically employing three of the five column-detector combinations. The first combination (abbreviated as 'DB5ms/MSD') was a DB-5ms column (J&W; 60 m, 0.25 mm I.D., 0.5 µm film thickness) output to a quadrupole mass spectrometer detector (MSD) (HP-5973). The second combination (Restek1701/ECD) was a RESTEK 1701 column (60 m, I.D. 0.25 mm, film 0.5 µm), which was output to an electron capture detector (ECD). A third combination (DB5-Restek1701/ECD) was a DB-5 (J&W 30 m, I.D. 0.25 mm, film 1 µm) column connected in series to a RESTEK 1701 column (5 m, I.D. 0.25 mm, film 0.5 µm), and output to an ECD. The DB5ms/MSD, Restek1701/ECD, and DB5-Restek1701/ECD combinations received 10.1%, 7.2%, and 6.8% of the sample flow, respectively. For PEM Tropics A, the best alkyl nitrate precision was obtained from the Restek 1701/ECD combination. For PEM-Tropics B, the best precision was obtained by averaging the data from the Restek 1701/ECD and DB-5MS/ECD combinations [Colman *et al.*, 2001]. During PEM-Tropics A, an ECD makeup gas that was 99.95% N₂(g) and 0.05% O₂(g) was employed. This technique, known as oxygen doping, significantly enhanced ECD sensitivity toward hydrogen containing halocarbons and organic nitrates. However, oxygen doping was not needed for PEM-Tropics B because the new HP 6890-based ECDs employed were roughly an order of magnitude more sensitive than the HP 5890 ECDs used for PEM-Tropics A [Colman *et al.*, 2001].

[10] The typical alkyl nitrate detection limit was 0.02 pptv (0.01 pptv for methyl nitrate) and precision ±5% at mixing ratios above 5 pptv and ±10% below 5 pptv [Colman *et al.*, 2001]. The detection limits for methyl iodide (CH₃I), bromoform (CHBr₃) and DMS are 0.01, 0.01, and 1 pptv, respectively. The precision for CH₃I and CHBr₃ were 3% and 2%, respectively for PEM-Tropics A, and 1.1 and 1.6%, respectively for PEM-Tropics B. For DMS, the precision is approximately 3% at mixing ratios >25 pptv, and 1 pptv or 15%, whichever is higher, at mixing ratios <10 pptv [Colman *et al.*, 2001; Simpson *et al.*, 2001].

[11] Routine alkyl nitrate calibration relied on the regular analysis of whole air working standards, which had been previously calibrated against a synthetic standard prepared at NCAR. The primary standard contained alkyl nitrates from C₁ to C₇ that were prepared from laboratory synthesized compounds or commercially available nitrates. A ppbv level standard was prepared in moist air by injection of a mixture of nitrates into a 35-liter stainless steel canister and pressurization to about 20 hPa. The nitrate levels in the mixture were calibrated by gas chromatography with flame ionization and atomic emission detection. Flow dilution of the primary standard to pptv levels was used to calibrate the secondary, whole air standard.

[12] We note that the sampling and analytical procedures used here do not measure multifunctional nitrate compounds; also tertiary nitrates are not detected with these procedures.

[13] In addition to our measurements [Simpson *et al.*, 2001], DMS measurements were also made in flight by isotopic dilution gas chromatography/mass spectrometry [Bandy *et al.*, 1993]. The detection limit for these DMS measurements was 1 pptv for PEM-Tropics A. All PEM-Tropics A and B measurements and merged data files are archived at NASA Langley Research Center and can be accessed via the GTE web site at <http://www-gte.larc.nasa.gov/orftp://ftp-gte.larc.nasa.gov/pub/>.

3. Results and Discussion

[14] The PEM-Tropics B field campaign was conducted from March to April 1999, with major deployment sites in Hawaii, Kiritimati (Christmas Island), Tahiti, and Fiji [Raper *et al.*, 2001]. The PEM-Tropics A field campaign is described by Hoell *et al.* [1999]. For both experiments, whole air samples were collected aboard the NASA Ames/Dryden DC-8 and the NASA Wallops P-3B research aircraft. Sample locations used in this analysis are displayed in Figure 1.

3.1. Latitudinal Distributions

[15] At low altitudes (0–2 km), MeONO₂ displays its highest mean mixing ratios (greater than approximately 15 pptv) along an equatorial band that stretches across the Pacific (Figure 2). This band spans a width of latitudes from about 8°N to about 13°S and is confined to an atmospheric mixing height of about 2 km (Figure 3). These data are consistent with the suggested oceanic source for this gas [Walega *et al.*, 1992; Atlas *et al.*, 1993], and with airborne measurements during the ACE-1 Pacific latitudinal profile [Blake *et al.*, 1999a]. Blake *et al.* [1999a] report similarly high concentrations (up to 50 pptv) of MeONO₂ in the marine boundary layer (MBL) over the equatorial Pacific near Christmas Island (1–3°N). A strong oceanic source may also contribute to the higher mixing ratios of methyl nitrate in the free troposphere of the South Pacific compared to the North Pacific background. The southern hemisphere is dominated by ocean surface and marine emissions may contribute to the larger atmospheric background of methyl nitrate. For example, above 2 km, mean methyl nitrate mixing ratios are typically between 5–8 pptv at southern latitudes (>10°S) but are only 3–4 pptv at latitudes 10°N (Table 1).

[16] The lowest mean MeONO₂ levels (<6 pptv) are observed to the north of the equatorial enhancements, with slightly higher levels (up to 12 pptv) to the south (Figure 2). The highest ethyl nitrate (EtONO₂) levels are found in the same equatorial band as for MeONO₂. However, EtONO₂ exhibits slightly higher mean mixing ratios to the north than to the south of this band.

[17] The highest 2-propyl nitrate (2-PrONO₂) mixing ratios (to 9 pptv) are located at the most northerly PEM-Tropics B latitudes and up to an altitude of about 5 km (Figures 2 and 3). Elevated 2-PrONO₂ mixing ratios (to 6 pptv) are also observed near the equator (Figures 2 and 3). 2-butyl nitrate (2-BuONO₂) also displays its highest levels (to about 10 pptv) in the northern hemisphere (NH), but almost no equatorial or southern hemisphere (SH) enhancement (Figures 2 and 3). Blake *et al.* [2001] report urban/industrial continental outflow associated with elevated

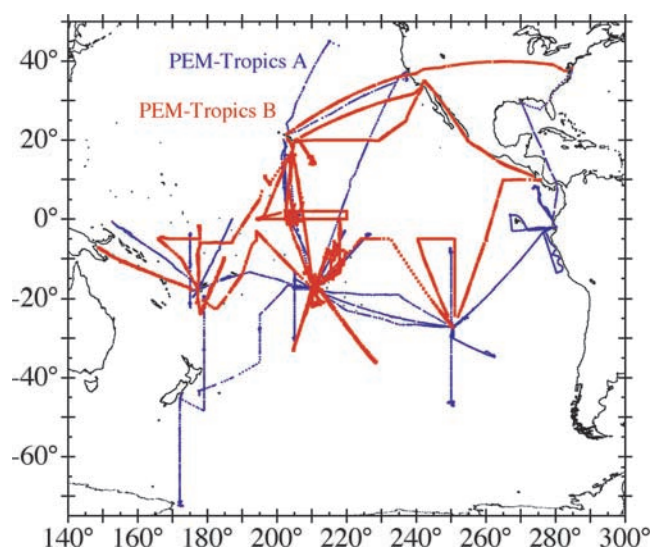


Figure 1. Location of whole air samples collected during NASA PEM-Tropics A (blue symbols) and PEM-Tropics B (red symbols).

levels of NMHCs (including the 2-PrONO₂ and 2-BuONO₂ precursors propane and n-butane) and other anthropogenic indicators at the same northern latitudes and altitudes as the highest 2-PrONO₂ and 2-BuONO₂ mixing ratios. Levels of all C₁-C₄ alkyl nitrates measured at latitudes near 20°N are consistent with seasonal distributions of alkyl nitrates at the Mauna Loa Observatory during the MLOPEX experiments [Atlas and Ridley, 1996].

[18] In addition, the mean mixing ratios of 2-PrONO₂ and 2-BuONO₂ are enhanced close to the coast of Central America (Figure 2). Fresh local biomass burning and urban emissions were noted in this region [Blake *et al.*, 2001]. Therefore, all data from DC-8 Flight 22 and part of DC-8 Flight 21 have been removed from the data subset hereafter referred to as “remote Pacific”.

3.2. Emission Signatures

[19] Figure 4 reveals good correlations over the remote Pacific in the NH (north of 10°N) between EtONO₂, 2-PrONO₂, and 2-BuONO₂ and the industrial tracer C₂Cl₄, strongly indicating co-located sources for the longer-chain alkyl nitrates and C₂Cl₄. This alkyl nitrate source is most likely to be in the form of urban/industrial emissions of NMHCs.

[20] After methyl nitrate (which has no significant correlation with C₂Cl₄), ethyl nitrate exhibits the lowest enhancement ratio (0.45 pptv/pptv of C₂Cl₄) (Figure 4) but has a very good correlation ($R^2 = 0.95$), suggesting that a small amount originates from NH urban/industrial emissions of NMHCs and subsequent transformations. In the SH, EtONO₂ shows no significant correlation to C₂Cl₄, supporting the hypothesis that the main equatorial/SH source is oceanic in origin. 2-Butyl nitrate has the highest enhancement (1.1 pptv/pptv of C₂Cl₄) but a relatively poor correlation ($R^2 = 0.72$). This gas is produced from its parent NMHC, n-butane [Roberts *et al.*, 1990, 1998], but 2-BuONO₂ has a shorter lifetime than EtONO₂ (and a much shorter atmospheric lifetime than C₂Cl₄), resulting in depleted levels after long-range transport for some samples shown in Figure 4.

[21] By contrast with the longer-chain alkyl nitrates, MeONO₂ remained at very low mixing ratios (less than 5 pptv) north of 10°N during PEM-Tropics B, with a mean value of 3.4 pptv (Table 1) and no correlation with C₂Cl₄ (Figure 4). Other trace gases known to have principally oceanic sources, CH₃I (Figure 4) and DMS (not shown), were also not correlated with C₂Cl₄ north of 10°N. Bromoform had a relatively poor, but significant correlation with C₂Cl₄ and a low enhancement ratio, suggesting that we encountered air masses with some small component from urban/industrial emissions of CHBr₃ north of 10°N (it is used in manufacturing as a cleaning solvent). However, natural sources of bromoform from oceanic emissions in northern latitudes can't be excluded [e.g., Yokouchi *et al.*, 1997].

[22] Ethyl nitrate is very well correlated with MeONO₂ ($R^2 = 0.98$) south of 10°N (Figure 5), indicating a tightly linked common (oceanic) source that is 3 times stronger for MeONO₂. 2-Propyl nitrate is also well correlated ($R^2 = 0.93$), but has a lower enhancement per molecule of

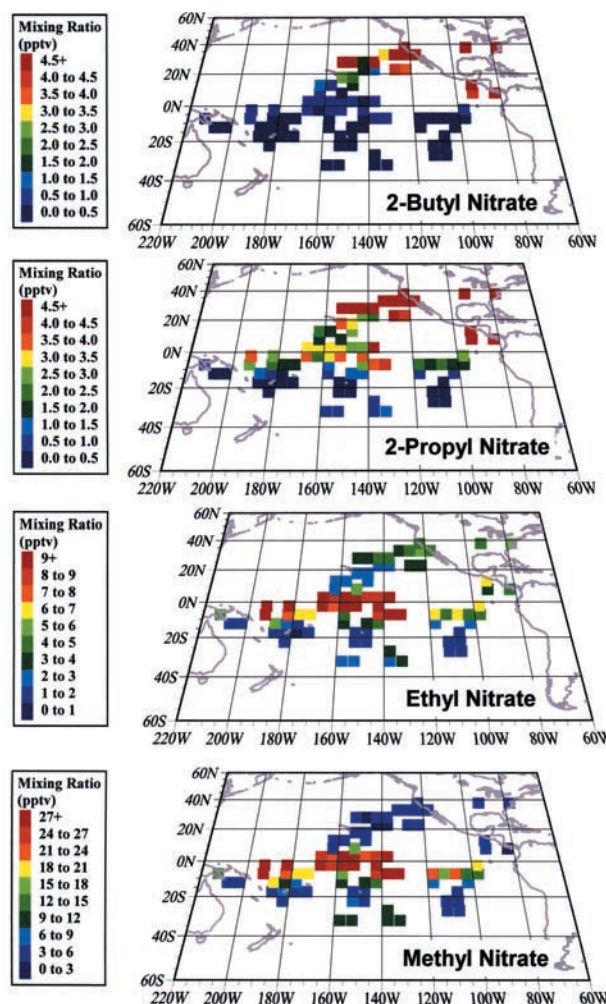


Figure 2. Spatial distribution of four C₁-C₄ alkyl nitrates in the lower troposphere (0–2 km) during NASA PEM-Tropics B. Each square or “patch” is color-coded to represent the mean mixing ratio over all samples collected in a 5°-5° latitude-longitude and 0–2 km altitude range.

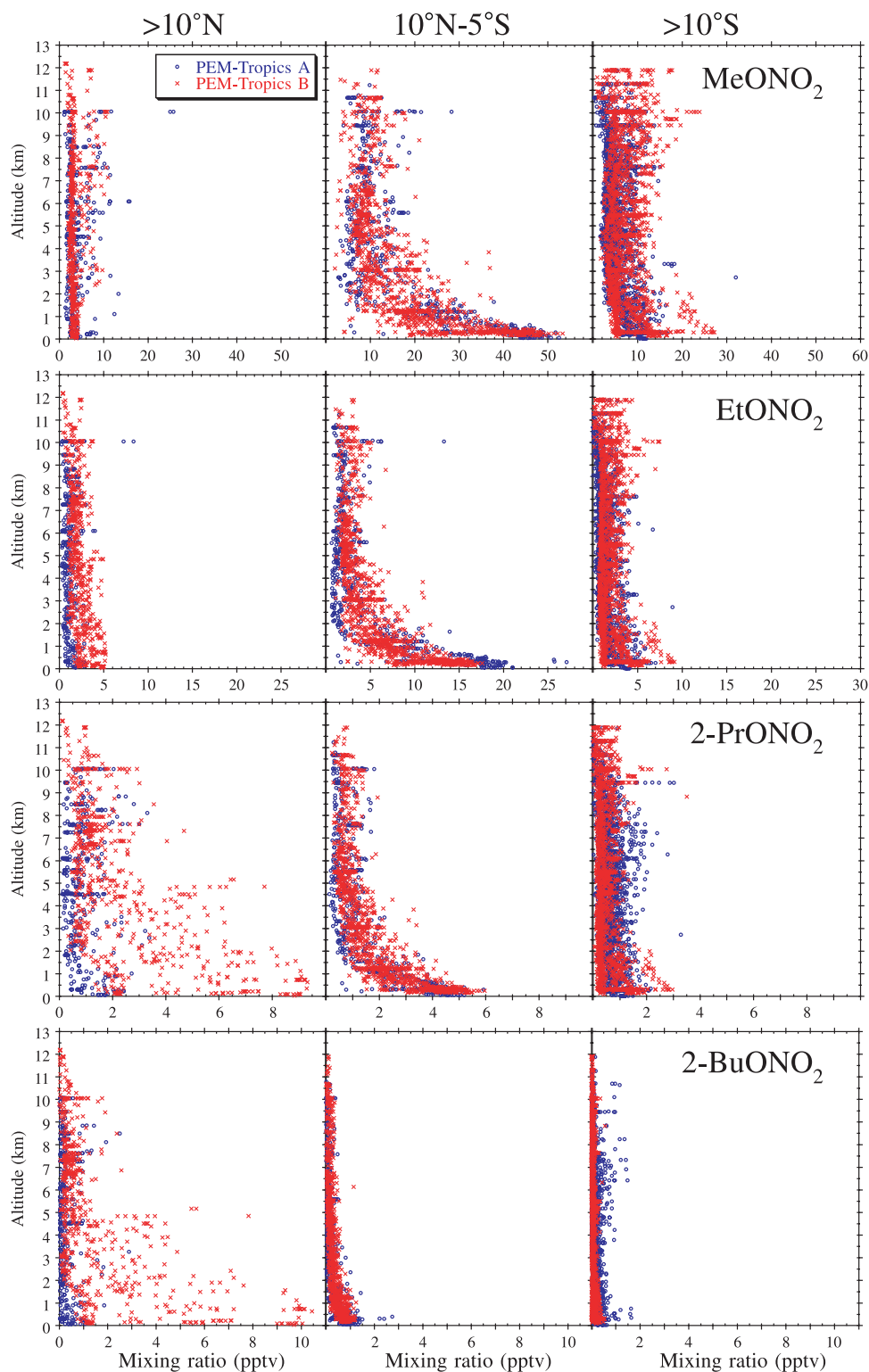


Figure 3. Vertical profiles of the light alkyl nitrates for 3 latitude ranges over the remote Pacific during NASA PEM-Tropics A and PEM-Tropics B.

MeONO₂ (ratio 1:10). 2-butyl nitrate is fairly well correlated with MeONO₂ ($R^2 = 0.60$), so also seems to have a small ocean source, but only one molecule of 2-BuONO₂ is emitted for approximately every 50 of MeONO₂ (Figure 5).

[23] Table 2 shows that the equatorial mixed layer alkyl nitrate correlations with MeONO₂ are remarkably similar

for both PEM-Tropics A and PEM-Tropics B. EtONO₂ versus MeONO₂ have the most similar slope and the best R^2 values. Bromoform has a similar, but somewhat higher correlation ratio versus MeONO₂ for PEM-Tropics B compared to A (Table 2). These observations are consistent with previous measurements in the Central Pacific by *Atlas et al.*

Table 1. Mixing Ratios (pptv) for Three Altitude and Three Latitude Ranges Over the Remote Pacific^a

	MeONO ₂		EtONO ₂		2-PrONO ₂		n-PrONO ₂		2-BuONO ₂		CH ₃ I		CHBr ₃		DMS		Propane	
	PTA	PTB	PTA	PTB	PTA	PTB	PTA	PTB	PTA	PTB	PTA	PTB	PTA	PTB	PTA*	PTB	PTA	PTB
<i>Latitudes > 10°N</i>																		
<i>8–12.2 km. N = 83, 111</i>																		
Median	2.8	3.2	1.2	1.6	0.84	0.96	0.05	0.17	0.16	0.29	0.07	0.11	0.38	0.42	<1	<1	34	35
Mean	4.3	4.1	1.4	1.7	0.99	1.08	0.08	0.20	0.27	0.41	0.08	0.12	0.38	0.41	1	<1	41	48
SD	4.1	2.3	1.2	0.8	0.62	0.68	0.11	0.15	0.40	0.42	0.04	0.05	0.18	0.18	7	<1	28	36
<i>2–8 km. N = 234, 418</i>																		
Median	3.2	2.9	1.0	1.8	0.61	1.26	0.07	0.26	0.17	0.52	0.08	0.11	0.37	0.44	<1	<1	20	49
Mean	4.0	3.4	1.1	2.1	0.76	1.85	0.09	0.36	0.28	0.96	0.11	0.13	0.39	0.45	2	<1	25	85
SD	2.5	1.5	0.6	0.8	0.58	1.38	0.09	0.28	0.35	1.19	0.09	0.08	0.17	0.15	4	1	19	77
<i>0–2 km. N = 90, 164</i>																		
Median	3.0	3.4	1.1	3.2	0.85	4.34	0.11	0.86	0.25	2.94	0.54	0.52	0.51	0.86	23	9	21	211
Mean	3.7	3.4	1.3	3.3	1.09	4.82	0.18	0.97	0.38	4.01	0.48	0.49	0.58	0.85	64	17	33	276
SD	2.0	0.5	0.7	1.1	0.69	2.60	0.17	0.53	0.34	3.15	0.25	0.18	0.30	0.26	107	25	27	222
<i>Latitudes 10°N–5°S</i>																		
<i>8–12 km. N = 81, 113</i>																		
Median	8.8	10.2	1.8	2.9	0.47	0.72	0.03	0.12	0.08	0.10	0.07	0.09	0.44	0.58	<1	<1	19	11
Mean	10.1	9.9	2.3	2.8	0.61	0.77	0.06	0.13	0.09	0.12	0.09	0.09	0.49	0.60	2	<1	19	15
SD	4.3	3.3	1.8	0.9	0.39	0.28	0.07	0.05	0.08	0.09	0.05	0.04	0.21	0.18	7	1	6	9
<i>2–8 km. N = 253, 531</i>																		
Median	8.4	9.6	1.8	2.8	0.72	0.93	0.07	0.17	0.12	0.20	0.07	0.11	0.53	0.66	<1	<1	17	13
Mean	9.5	11.2	2.1	3.3	0.80	1.03	0.10	0.18	0.16	0.21	0.09	0.12	0.57	0.70	5	4	18	15
SD	4.0	5.0	1.2	1.5	0.42	0.51	0.11	0.09	0.13	0.13	0.06	0.06	0.24	0.26	11	11	7	10
<i>0–2 km. N = 258, 554</i>																		
Median	35.1	26.0	11.5	8.8	3.42	3.19	0.51	0.57	0.56	0.66	0.35	0.37	1.59	1.86	58	75	14	17
Mean	33.5	28.3	12.0	9.4	3.16	3.21	0.51	0.56	0.60	0.62	0.34	0.35	1.57	1.86	59	73	17	20
SD	11.3	11.3	5.5	3.8	1.19	1.20	0.28	0.23	0.37	0.25	0.12	0.15	0.53	0.70	34	54	18	10
<i>Latitudes > 10°S</i>																		
<i>8–12 km. N = 454, 497</i>																		
Median	4.3	7.6	0.9	1.7	0.35	0.34	0.02	0.05	0.04	0.04	0.06	0.08	0.30	0.42	<1	<1	24	5
Mean	4.9	8.1	1.0	1.9	0.42	0.45	0.02	0.06	0.08	0.05	0.06	0.09	0.34	0.43	<1	<1	27	5
SD	2.6	4.0	0.6	1.2	0.37	0.39	0.03	0.06	0.16	0.06	0.04	0.07	0.23	0.21	2	1	16	3
<i>2–8 km. N = 1366, 840</i>																		
Median	4.6	5.8	1.1	1.4	0.54	0.35	0.05	0.06	0.08	0.06	0.06	0.10	0.44	0.42	<1	<1	24	5
Mean	5.2	6.6	1.3	1.6	0.63	0.42	0.06	0.07	0.13	0.08	0.08	0.12	0.46	0.44	1	2	26	6
SD	2.5	2.9	0.8	0.8	0.36	0.25	0.06	0.04	0.16	0.06	0.06	0.08	0.23	0.14	5	10	11	5
<i>0–2 km. N = 378, 445</i>																		
Median	8.3	7.3	2.4	2.1	0.77	0.60	0.12	0.11	0.22	0.11	0.37	0.44	0.92	0.70	12	33	23	5
Mean	8.8	9.2	2.7	2.7	0.85	0.78	0.14	0.14	0.28	0.14	0.35	0.46	0.95	0.69	21	73	26	5
SD	2.6	5.1	1.2	1.8	0.36	0.61	0.08	0.10	0.22	0.10	0.16	0.18	0.31	0.22	32	88	12	3

^aComparison of PEM-Tropics A (PTA) with PEM-Tropics B (PTB). N, no of UCI whole air samples collected during PTA and PTB, respectively. Asterisk indicates Drexel in-situ DMS data merged to whole air sample time base.

[1993], who found that the equatorial maxima of EtONO₂ and 2-PrONO₂ were related to maxima in brominated hydrocarbons, as well as chlorophyll and nitrate (which are oceanographic indicators of enhanced marine productivity and upwelling).

[24] Although remote MBL alkyl nitrate mixing ratios are well correlated with each other and with CHBr₃, suggesting a common oceanic emission mechanism, CH₃I and DMS are not closely correlated with MeONO₂ (Table 2 and Figure 5). This wide spatial variability in mixing ratios of ocean source gases is illustrated by the vertical profiles of MeONO₂, CHBr₃, DMS, and CH₃I from a single DC-8 flight (Flight 12 from Fiji and back) on March 25 1999 (Figure 6). As in Figure 5, MeONO₂ and CHBr₃ show similar relative distributions. Even then, the far south profile in Figure 6 (at 18°S) is greatly enhanced in CHBr₃ for the lowest altitude sample compared to MeONO₂. (See also oceanic emission fluxes calculated by S. Oncley (manuscript in preparation, 2002). Close correlation of tracers from ocean sources depends on common oceanic production mechanisms, saturation state, and specific source dis-

tributions. For example, while MeONO₂ has a maximum over the equator, CH₃I tends to show boundary layer maxima at latitudes both north and south of the equator. Similarly, DMS production depends on emissions of precursors from certain plankton species that may not be related to the same processes that contribute to emissions of alkyl nitrates.

[25] For compounds with a common surface source, vertical profiles of different gases should reflect something about their respective chemical lifetimes. It follows that a measure of the relative lifetimes might be a comparison of BL to FT concentrations. MeONO₂ and CHBr₃ have lifetimes on the order of 15–30 days (nominally), but CH₃I is much shorter (2–4 days), and DMS has a lifetime of only a few hours. Indeed, the black profile at 5°S on Figure 6 illustrates this lifetime dependence, with the presence of marine cumulus providing shallow convection up to 1.5 km, then mixing ratios falling in the order MeONO₂ & CHBr₃, CH₃I, DMS. However, the blue profile at 5°S (Figure 6) shows that BL/FT ratios for CH₃I, MeONO₂, and CHBr₃ are all fairly similar, except for DMS. Table 1

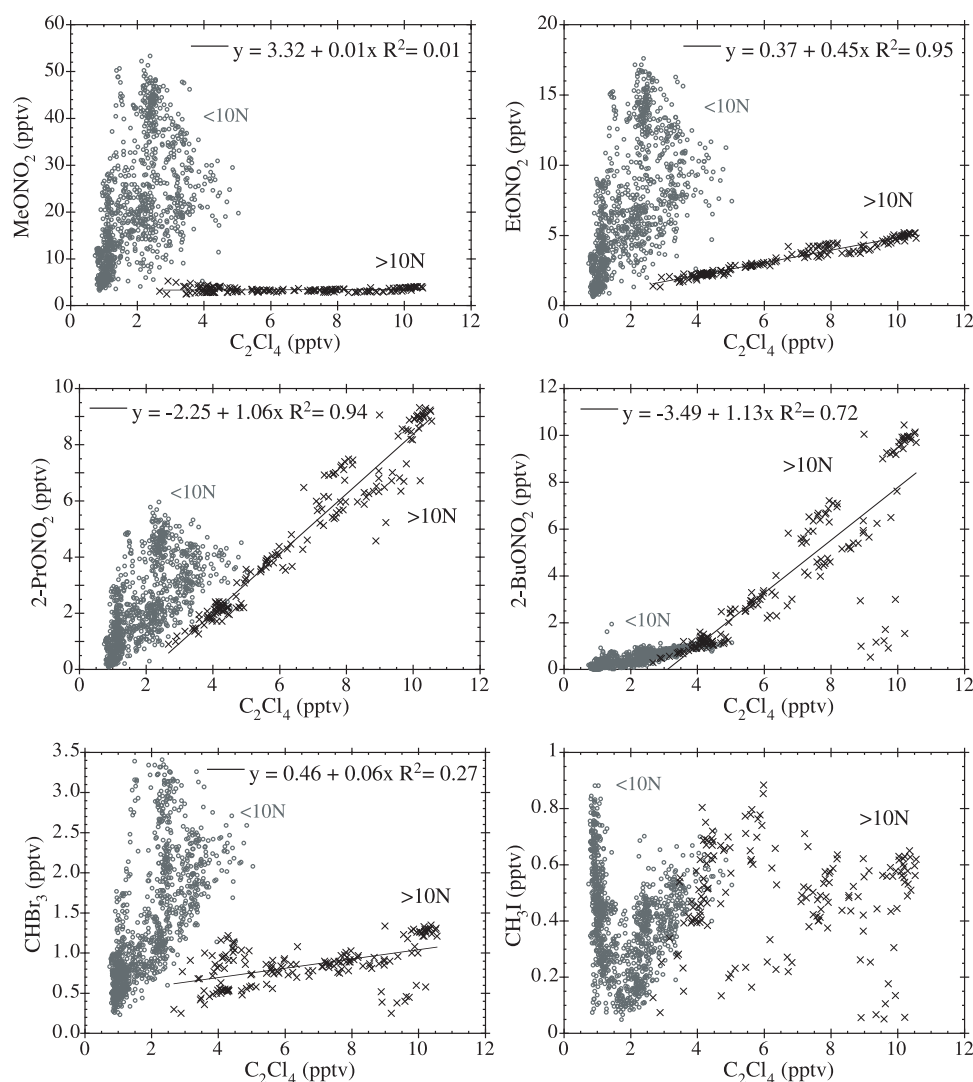


Figure 4. Correlation plots of light alkyl nitrates, CHBr_3 , and CH_3I with C_2Cl_4 at altitudes <2 km over the remote Pacific during NASA PEM-Tropics B.

also reveals similar ratios for averaged equatorial data in the <2 km bin compared to 2–8 km for CH_3I , MeONO_2 , and CHBr_3 , but higher values for DMS. The difference between these two 5°S profiles is that the blue profile was influenced by recent convection up to at least 6 km, as evidenced by the DMS enhancements visible to this altitude. Figure 7 reveals that a high incidence of rainfall, corresponding to a southern branch of the ITCZ, was observed near 5°S – 10°S during PEM-Tropics B, illustrating the important role played by convection in this region of the atmosphere. Comparison of the profiles and lifetimes may be able to highlight convective outflow and indicate the speed of ascent and merits future investigation, including studying the role of horizontal transport, which may also play a significant role.

3.3. Ocean-Atmosphere Flux of N

[26] Another potentially interesting aspect of the emission of alkyl nitrates from the surface ocean is that it results in a local loss of some nutrient N from the ocean to the atmosphere. Oxidation will presumably return the N to the sea surface, but at some location distant from the source.

[27] If we assume steady state loss of C_1 – C_4 alkyl nitrates then;

$$\text{Average mixing ratio} \times \text{BL height} \times \text{loss rate} = \frac{\text{Amount}}{\text{lost/area/day}}$$

From this we estimate a contribution to the lower 2 km of the equatorial Pacific of $\approx 2.43 \mu\text{g N/m}^2/\text{day}$ ($= 0.89 \text{ mg N/m}^2/\text{yr}$) based on PEM-Tropics B mixing ratios (Table 1) and calculated lifetimes with respect to photolysis and reaction with OH and Cl radicals. Typical wet deposition of NO_3^- is in the range of 8–43 $\text{mg N/m}^2/\text{y}$ [Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP), 1989] and comparable sedimentation loss of N from the euphotic zone is on the order of total N inputs. Thus, this atmospheric loss is small relative to sources of NO_3^- to the ocean (for example from rainwater). Our calculated atmospheric NO contribution from photochemical aging of alkyl nitrates is almost double the $0.52 \text{ mg N/m}^2/\text{yr}$ estimated for the central equatorial Pacific for the NO flux attributed to solar photolysis of nitrite ion [Zafrou and McFarland, 1981]. Schultz et al. [1999] reported that the long range transport of

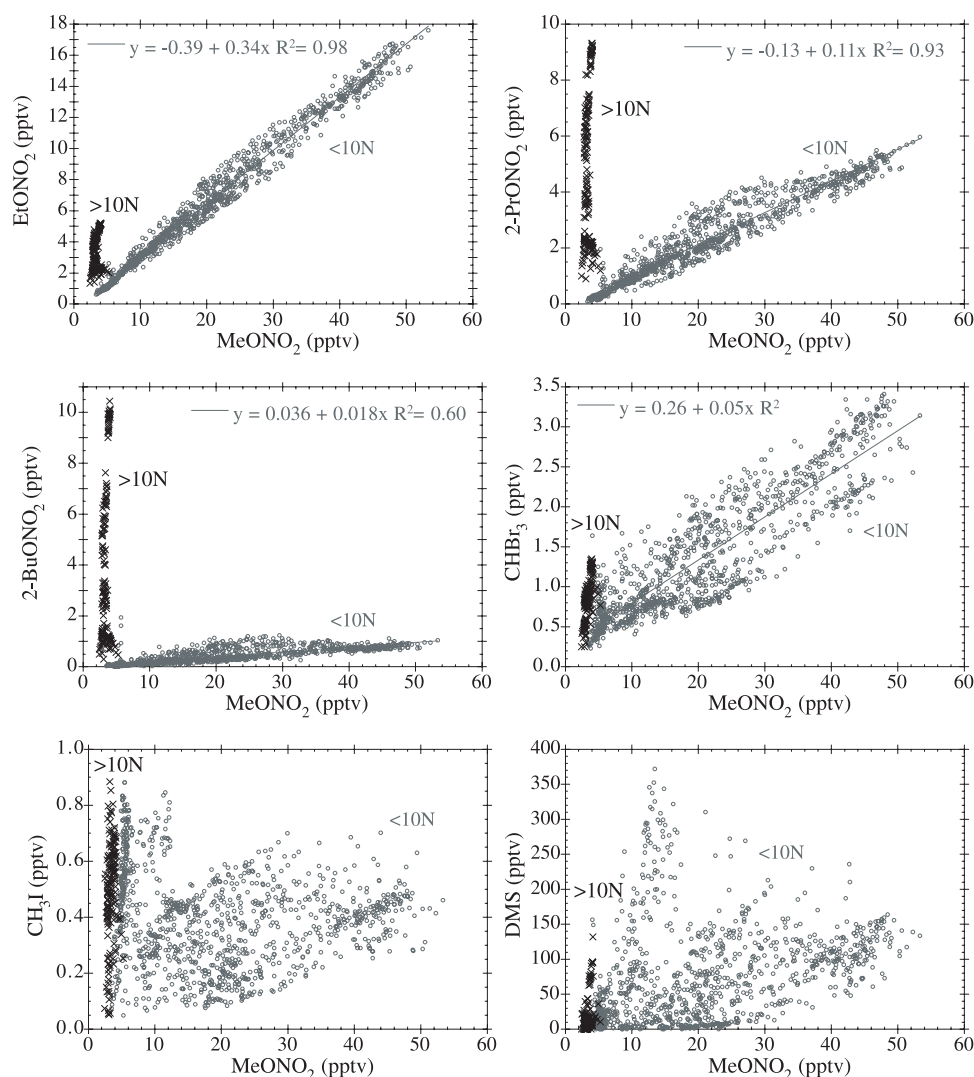


Figure 5. Correlation plots of light alkyl nitrates, CHBr_3 , CH_3I , and DMS with MeONO_2 at altitudes <2 km over the remote Pacific during NASA PEM-Tropics B.

PAN (from southern hemisphere biomass burning) and its subsequent thermal decomposition at low altitudes was the dominant source of NO_x to the remote atmosphere over the equatorial South Pacific during PEM-Tropics A. Below 2 km, Schultz et al. estimated methyl nitrate photolysis to contribute only about 6% to NO_x production, with loss of HNO_3 (by photolysis and OH reaction) contributing about 10%. However, it has recently been suggested that the mixing ratios of PAN that were encountered during both PEM-Tropics A and B were so frequently below instrument detection limits as to skew any calculations performed employing only the above LOD subset of data in favor of

overestimating the role played by PAN in the remote marine boundary layer NO_x budget [Olson et al., 2001].

3.4. Comparison of PEM-Tropics A and B

[28] During PEM-Tropics B the ITCZ in the Pacific Basin was not well defined. As can be seen from Figure 7, two zonal bands of convection were usually observed, one on either side of the equator at 5° – 10°N and 5° – 10°S [Fuelberg et al., 2001; Hu et al., 2001; Avery et al., 2001]. This is typical for March–April [Hu et al., 2001]. Convective activity during this period appeared to alternate between these branches of the ITCZ in the NH and the SH [Hu et al.,

Table 2. Correlation Slopes and R^2 Values for C_1 – C_4 Alkyl Nitrates and CHBr_3 Versus MeONO_2 During PEM-Tropics A (PTA) and PEM-Tropics B (PTB) for Samples Collected South of 10°N and Below 2 km Over the Remote Pacific

	EtONO_2		2-PrONO_2		$n\text{-PrONO}_2$		2-BuONO_2		CHBr_3	
	PTA	PTB	PTA	PTB	PTA	PTB	PTA	PTB	PTA	PTB
Slope	0.39	0.34	0.09	0.11	0.016	0.020	0.015	0.018	0.031	0.054
R^2	0.94	0.98	0.93	0.93	0.74	0.88	0.39	0.60	0.70	0.80

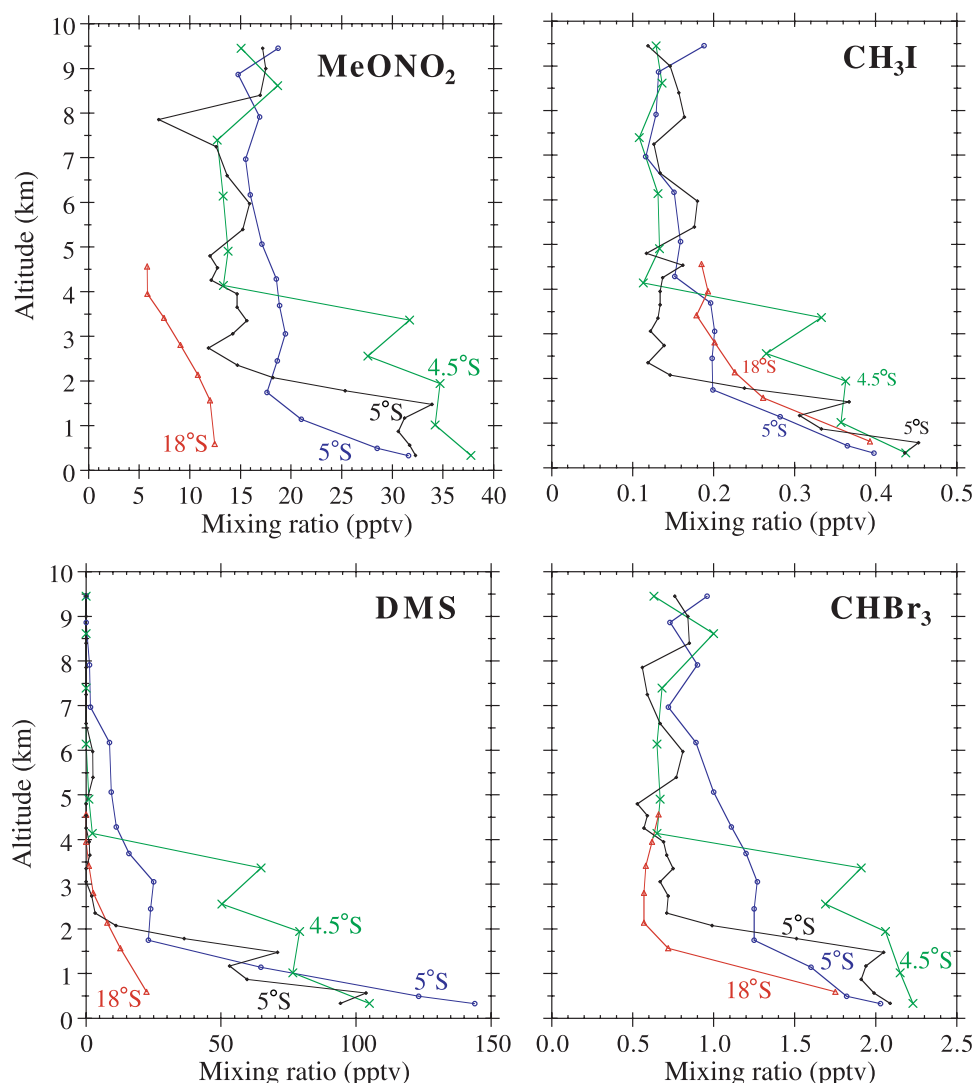


Figure 6. Vertical profiles sampled during Fiji local DC-8 Flight 12 as part of PEM-Tropics B.

2001]. March average rainfall rates were higher for the southern branch than those for April (Figure 7). By contrast, tropical rainfall associated with the ITCZ was confined to a more idealized single solid band at 5° – 10° N during PEM-Tropics A (Figure 7). As a result of the better-defined ITCZ during PEM-Tropics A, deep convection associated with that convergence was much stronger and persistent than Tropics B [Fuelberg *et al.*, 2001].

[29] Despite the different convective conditions, remarkably similar levels of MeONO_2 were observed during both PEM-Tropics A and B for all latitude and altitude ranges (Figures 3 and 8 and Table 1). At equatorial latitudes, median PEM-Tropics A and B levels were also comparable for all the measured alkyl nitrates and CH_3I , CHBr_3 , DMS, and propane (Table 1 and Figure 3). The equatorial enhancements of MeONO_2 were greatest at low altitude (<2 km) but persisted to the highest sampling altitudes as the result of fast equatorial convection associated with the ITCZ (Figures 7 and 8), suggesting that MeONO_2 is a useful marker for high altitude air masses of marine equatorial origin. Even though the maximum ITCZ convection is not co-located with the maximum equatorial marine bound-

dary layer mixing ratios, Figure 8 shows that equatorial marine boundary layer air enhanced with MeONO_2 is frequently entrained into ITCZ convection (consistent with Hu *et al.* [2001]). The active southern branch of the ITCZ (Figure 7) appears to have contributed to the slightly higher mixing ratios of MeONO_2 observed in the upper troposphere south of the equator during PEM-Tropics B compared to PEM-Tropics A (Figure 8). In fact, MeONO_2 is quite consistently enhanced above background levels up to the DC-8 flight ceiling altitude of 12 km in the free troposphere near the equator, especially for PEM-Tropics B. Using CH_3I as a marine tracer (which also exhibits enhanced free tropospheric mixing ratios), Wang *et al.* [2001] suggest that the observed vertical distribution implies stronger outflow in the middle troposphere than predicted using current general circulation models. In a further study designed to improve such regional and global model parameterizations, Pickering *et al.* [2001] describe a cloud-resolved model simulation of a strong tropical marine SPCZ (South Pacific Convergence Zone) convection event that was sampled near 17°S during PEM-Tropics B. They employ measured CH_3I , CO and O_3 as tracers for upward

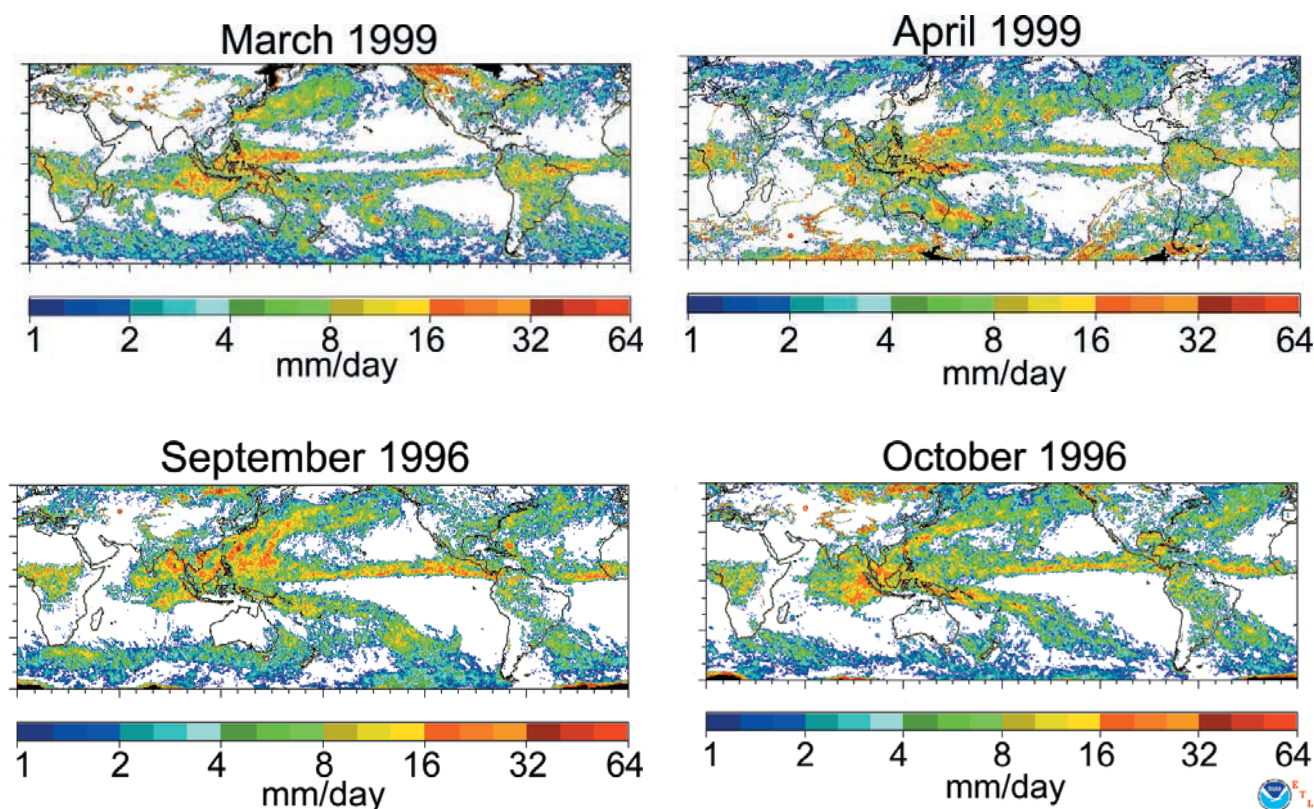


Figure 7. Global rainfall rates derived using the Ferriday algorithm on SSM/I satellite data. Average rainfall rates during (a) March and (b) April 1999 (during PEM-Tropics B); (c) September and (d) October 1996 (during PEM-Tropics A). Note the single band of rainfall indicating the position of the ITCZ just north of the equator during PEM-Tropics A, and the double structure of the ITCZ each side of the equator during PEM-Tropics B. These images were downloaded from the NOAA Environmental Technology Laboratory climate image archive at <http://www.etl.noaa.gov/satres/archive.html>.

transport of marine boundary layer air. According to this simulation, the cloud reached a height of about 16 km, with an overshooting top to nearly 18 km. Elevated CH_3I mixing ratios were predicted up to about 16 km, with maximum values near 12 km that agreed quite well with observations. MeONO_2 was not enhanced at altitude during this event because the convection inflow occurred in an area where its boundary layer concentration was relatively low. However, employing MeONO_2 for this type of analysis of deep ITCZ convection may help to improve cloud parameterizations as well as understanding of stratosphere-troposphere exchange. Measurements of MeONO_2 would be a useful addition to CH_3I as a diagnostic of ITCZ convection. Sampling at altitudes above 12 km is needed to confirm whether mixing ratios of such gases increase above 12 km in ITCZ outflow, which reaches altitudes of approximately 14–18 km.

[30] North of about 10°N MeONO_2 levels are very low for both PEM-Tropics A and B (Figure 8), suggesting that MeONO_2 had no significant NH continental sources during either PEM-Tropics measurement period. Another large section in Figure 8 that exhibited very low MeONO_2 mixing ratios is in the southern tropical mid-upper troposphere (above about 4 km) during PEM-Tropics A. PEM-Tropics A was flown at a time when this region of the atmosphere was strongly influenced by aged biomass burning plumes [Blake *et al.*, 1999b], so the fact that

MeONO_2 levels are so low suggests that the transport of MeONO_2 from biomass burning is minimal. Median mixing ratios of both 2- PrONO_2 and 2- BuONO_2 were very low (<1 pptv) in the SH during both PEM-Tropics A and B (Table 1), but Figure 3 shows that peak PEM-Tropics A values were somewhat higher than for PEM-Tropics B. These small PEM-Tropics A enhancements could result from the influence of biomass burning. By contrast, the PEM-Tropics B field campaign took place in the southern-tropical wet season, when the influence from biomass burning was minimal.

[31] PEM-Tropics A reached much further south during flights that were based out of New Zealand (Figure 1). These most southerly data reveal slightly elevated levels of MeONO_2 at low and mid-altitudes (Figure 8). These observations are consistent with the enhanced MeONO_2 concentrations (up to 30 pptv) observed previously over polar waters south of Tasmania during December 1995 [Blake *et al.*, 1999a]. They are also consistent with high MeONO_2 and EtONO_2 seen on the coast of Antarctica by Jones *et al.* [1999].

[32] Both equatorial Pacific and southern polar waters are regions characterized by upwelling of high nutrient waters. However, only some of the nutrients transported to the surface by upwelling are taken up by photosynthesis, allowing chlorophyll levels to remain relatively low, so are known as high-nutrient, low-chlorophyll (HNLC) eco-

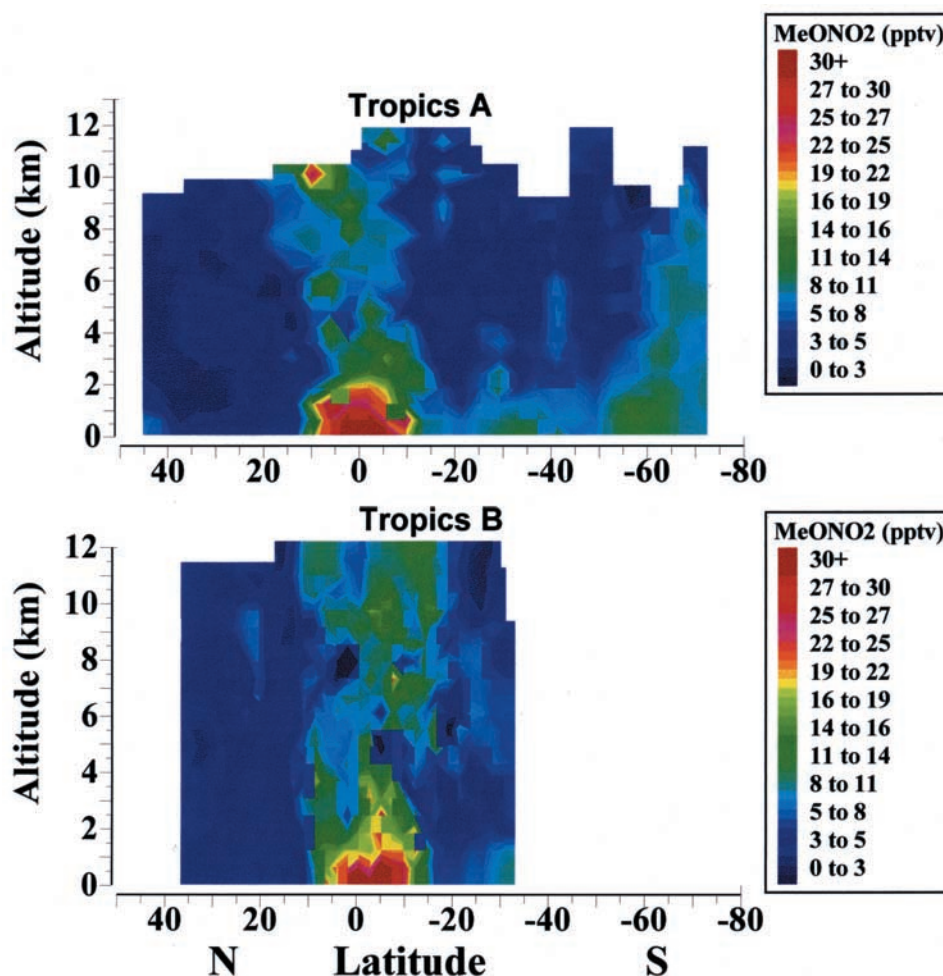


Figure 8. Latitude/altitude contour plots of methyl nitrate over the Central Pacific during NASA PEM-Tropics A and PEM-Tropics B for several PEM-Tropics A and PEM-Tropics B flights selected to represent a “curtain” through the Central Pacific.

systems. These nutrients persist in the surface layer because the production of phytoplankton is known to be limited by the supply of the trace nutrient iron [Cullen, 1991; Landry *et al.*, 1997; Coale *et al.*, 1996]. Fe concentrations tend to be highest in waters close to continental landmasses, which are comparatively rich in Fe, and from Fe-enriched atmospheric dust. Atmospheric dust deposition in the two major HNLC areas, the equatorial Pacific and Antarctic oceans, are the lowest in the world [Prospero, 1981; Uematsu, 1987]. It appears that in these HNLC waters, a lack of Fe availability selects a flora dominated by small cells which efficiently recycle nitrogen as NH_3 and strongly constrain the annual utilization of NO_3 , leaving the system persistently rich in major nutrients [Miller *et al.*, 1991]. We suggest that a portion of this excess NO_3 (or perhaps nitrite) may be transformed (either photochemically, or biogenically by biota which are specially adapted to these specific conditions) into alkyl nitrates or their precursors. The link between HNLC waters, which can be independently defined by satellite measurements of chlorophyll and by routine measurements of oceanic nitrate, and alkyl nitrates may facilitate calculations to better estimate the large-scale influence of alkyl nitrates on the atmospheric chemistry of these remote ocean regions.

[33] In the springtime NH troposphere sampled during PEM-Tropics B, mixing ratios of $\text{C}_2\text{-C}_4$ alkyl nitrates were very much higher (3–12-fold) at low-mid altitudes compared to summertime PEM-Tropics A (Table 1). This alkyl nitrate increase is consistent with the seasonal increase for their NMHC precursors reported by Blake *et al.* [2001] and with the seasonal data from Mauna Loa [Atlas and Ridley, 1996]. E.g., the 2-PrONO₂ precursor, propane, exhibits a 10-fold increase (see also Table 1). NMHCs build up at high latitudes during the winter months when sunlight, and therefore OH, are minimized. In springtime, strong easterly continental outflow transports these and other continental pollutants long distances across the North Pacific [Blake *et al.*, 1997, 2001]. Previous observations of alkyl nitrates at high latitudes support a winter build-up of alkyl nitrates along with NMHCs [Beine *et al.*, 1996; Swanson *et al.*, 2002].

[34] Low mixing ratios of n-PrONO₂ compared with 2-PrONO₂ in Table 1 reflect its lower chemical formation yield [Atkinson *et al.*, 1982]. The fact that the low altitude 2-PrONO₂:n-PrONO₂ ratios remain close to 6:1 for all 3 latitude bands in Table 1 indicate a similar (photochemical) formation mode for both the equatorial oceanic source and the Northern Hemisphere industrial source.

4. Conclusions

[35] The spatial distributions of light alkyl nitrates are remarkably similar for both the September–October 1996 PEM-Tropics A and March–April 1999 PEM-Tropics B. The consistently high equatorial mixing ratios observed provide the strongest evidence yet to establish the ocean as the major source for MeONO₂. Further, these results support the suggestion that CH₃I, CHBr₃, and DMS emissions are not necessarily coupled to the emission of biogenically produced C₁–C₃ alkyl nitrates. We suggest a link between our equatorial findings and the enhanced MeONO₂ concentrations observed previously over the other major area of high nutrient-low chlorophyll waters, the Southern Ocean around Antarctica. Integrating these observations with HNLC regions, as defined by satellite measurements of chlorophyll and oceanic nitrate analysis, may assist calculations that better assess the large-scale influence of ocean-source alkyl nitrates on the remote atmosphere.

[36] Ethyl nitrate has a dominant oceanic source in equatorial regions, but at mid NH latitudes a small additional source is associated with urban/industrial emissions. The low altitude distribution of 2-PrONO₂ appears to be almost equally influenced by equatorial oceanic and by anthropogenic NH emissions. Similar equatorial MBL mixing ratios were observed for both PEM-Tropics A and B, so no seasonal factors (which are minimal at the equator) were apparent. These stable oceanic emission factors may make a useful diagnostic for air masses that have recently been at low altitude over the equatorial Pacific Ocean, compared to the much lower EtONO₂:MeONO₂ ratios typically observed in air masses which have been influenced by urban/industrial emissions. The high 2-PrONO₂:MeONO₂ and 2-BuONO₂:MeONO₂ ratios for the corresponding anthropogenic-influenced NH air masses also provide a useful air mass characterization signature.

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